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Jeffrey D. Mills (PRSP), "Hydrocarbon Fuels Optimization"

2001 JANNAF – PDCS Meeting **(Statement A)**
(Colorado Springs, CO, 24-28 Sept 2001) (Deadline: PAST!!!)

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ABSTRACT

Hydrocarbon fuel performance in rockets is systematically considered using standard equilibrium, isentropic, one-dimensional computer codes with a new web-based interface. For reference engine conditions the optimized specific impulse depends only upon the mass-normalized (specific) enthalpy content and the hydrogen-to-carbon ratio. In this context promising families of strained and unsaturated high-energy hydrocarbon fuels, with special emphasis upon those currently under development by in-house researchers, are insightfully compared and justified. A variety of simple, mission-tailored metrics approximating payload mass gains and the relative importance of fuel density are considered with special application to similar kerosene fuels. In this way it is possible to begin to simply, if approximately, quantify some of the performance trade-offs among the relevant liquid-fuel physical and chemical properties and to easily screen a great number of possible fuels as a foundation for calculations employing more sophisticated and realistic rocket models.

INTRODUCTION

Enthalpy content is well known as a critical parameter for the performance of rocket fuels. Searches for improved fuels are therefore generally conducted among high-energy molecules. Fixed enthalpy thresholds have even sometimes been employed to screen prospective fuels. Perhaps less well appreciated, at least at a quantitative level, are the roles played by the atomic composition and density of the fuels. The optimum, theoretical performance of a hydrocarbon fuel burned with liquid oxygen (and using the simplest common rocket model) is completely determined by only its specific enthalpy of formation and the mole ratio of hydrogen and carbon atoms in the fuel. Therefore, in this simple context, the trade-offs between enthalpy content and atomic composition can be quantitatively determined and the promise and limitations of the chemical transformations represented by families of similar molecules can be elucidated.

As intimated by the exponential dependence of mass ratio upon specific impulse in the rocket equation, small changes in specific impulse can be magnified into large changes in mission parameters for a rocket. Without performing a specific mission analysis for each propellant combination, it might be useful to have available a variety of simple metrics, derived either from approximate analytic expressions or representative system-and mission analyses, to approximately quantify the effect of a higher performing fuel. Similar performance metrics involving density can also be explored, compared, and expanded. The account which follows is devoted to seeking to display in a convenient manner the approximate mission-specific performance trade-offs among the minimal set of determinative hydrocarbon characteristics, not with the goal of trying to substitute approximate, and ultimately probably inadequate, performance metrics for the detailed and exhaustive systems analyses necessary to confidently recommend a new propellant, but rather to promote a general understanding and justification of some of the results thereby obtained and to allow prescreening of whole data bases of prospective molecules, some of which may be at present barely known or ill-characterized, in preparation for such analyses.

RESULTS AND DISCUSSION

Web-Based, Graphical Interface to CEA

The CEA (Chemical Equilibrium and Applications) code of B. McBride and S. Gordon[1,2,3] at NASA-Glenn is a standard tool for the characterization of a number of combustion problems, including simple rocket performance. However, as presently distributed, it lacks built-in graphical capabilities, operating instead through a simple, albeit universal, command line interface.

In an effort to avoid the operating-system and hardware incompatibility and instability issues sometimes plaguing graphical suites as well as the labor of maintaining multiple versions of an evolving code, the present author has created a web-based, graphical front-end to CEA which places the maintenance burden upon a single Linux server. A number of modules, coded mostly in Perl and designed to support the widest variety of browser versions, take data from the user, construct input files for CEA, run calculations, and present the results in a user-friendly format. Its modular orientation also allows the easy incorporation of a number of simple "helper" utilities, most notably an SQL-compliant data base. Avenues for making this suite publicly available are currently being pursued and the author invites contact from those interested.

Reference Template for the Specific Impulse of Hydrocarbon Rocket Fuels

If, as an approximation to real rocket performance, one uses the results of a calculation assuming one-dimensional, adiabatic, equilibrated, and isentropic flow,[4] and if, further, a single oxidizer and set of representative rocket conditions (chamber pressure and exit and nozzle parameters) are chosen so as to allow comparison of different fuels in a common bipropellant basis, then the specific impulse of a fuel depends only upon its specific (mass-normalized) enthalpy content, its relative atomic composition, and its mixture ratio with the oxidizer. The number of independent parameters can be further reduced by one if, in the interests of attempting to gauge the maximum intrinsic potential of the fuel in the propellant, the mixture ratio is set to that which provides the optimum specific impulse. It must be admitted that the preceding approximations and constraints neglect not only many other practically important chemical and physical properties of the fuel itself, but also many of the adjustable design parameters of rocket engineering. Nevertheless, viewing a fuel as merely a packet of energy and chemical mass in isolation, one might hope to have stripped it to its most important performance-determining essentials.[5]

Even though these ideas could be extended to a number of fuel/oxidizer combinations, the present paper is primarily concerned with hydrocarbon performance optimized against liquid oxygen. In such a case the specific impulse would constitute a surface in a three-dimensional space, dependent only upon, for example, fuel enthalpy of formation and the molar ratio of hydrogen to carbon. To aid in visualization, this surface could be projected into the plane of the two independent parameters through the use of contours of constant performance (or "iso-I_{sp} lines"). This can be seen in Figures 1 and 2 for two sets of operating conditions commonly[6] used to at least initially assess and compare bipropellant rocket fuels with the position of RP-1 included for reference. These conditions are defined by the parameters in the titles to the figures and will be referred to hereafter as "sea-level" and "vacuum expansion." It should perhaps be further emphasized that

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[1] S. Gordon and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. I. Analysis," *Reference Publication*, No. NASA/RP-1311, Lewis Research Center, Cleveland OH, Oct. 1994.

[2] B.J. McBride and S. Gordon, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. II. Users Manual and Program Description," *Reference Publication*, No. NASA/RP-1311, Lewis Research Center, Cleveland OH, June 1996.

[3] See also: www.grc.nasa.gov/www/CEAWeb.

[4] G.P. Sutton, *Rocket Propulsion Elements: An Introduction to the Engineering of Rockets*, Sixth Ed., (Wiley, New York, 1992), pp. 41-88.

[5] While, to the author's knowledge, the exact formulation of this problem in terms of the independent parameters and arrangement of fuels in the following figures is unique (and was conceived of independently), not surprisingly, these sorts of considerations have a long history. See, *e.g.*, J.N. Wilson, "High Energy Hydrocarbon Booster Fuels," *Final Report*, S-14014 NASA-CR-72438, Contract No. NAS 7-410, Oct. 1965-Sept. 1966, Shell Development, Emeryville CA, pp. 12-25, J.J. Notardonato, P.A. Masters, "High Density Propellants for Single Stage to Orbit Vehicles," *Technical Memorandum*, No. NASA/TM X-73503, Lewis Research Center, Cleveland OH, 1976, J.W. Frankenfeld, T.W. Hastings, M. Lieberman, and W.F. Taylor, "High Performance, High Density Hydrocarbon Fuels," *Technical Report*, S-14014 NASA CR-159480, Exxon/Grus. 1KWD.78, Contract No. NAS 3-20394, Oct. 1978, Exxon Research and Engin., Linden NJ, p. 10, D.C. Rapp, "High Energy-Density Liquid Rocket Fuel Performance," *Twenty-Sixth Joint Propulsion Conference*, Paper No. AIAA 90-1968, Orlando FL, July 16-18, 1990, and E.J.

[6] F.C. Gunderloy, "Theoretical Performance of Rocket Propellant Combinations," *Poster*, Rockwell International, Rocketdyne Div., Advanced Programs, Canoga Park CA, Febr. 1988.

within the described approximations and for these conditions. Figures 1 and 2 completely characterize liquid-oxygen-optimized performance for all hydrocarbons, known or unknown; provided that the specific enthalpy of formation and average-hydrogen-to-carbon ratio can be determined, or at least approximated, the optimum specific impulse for any pure or mixed hydrocarbon fuel can be simply read from these plots by interpolation.

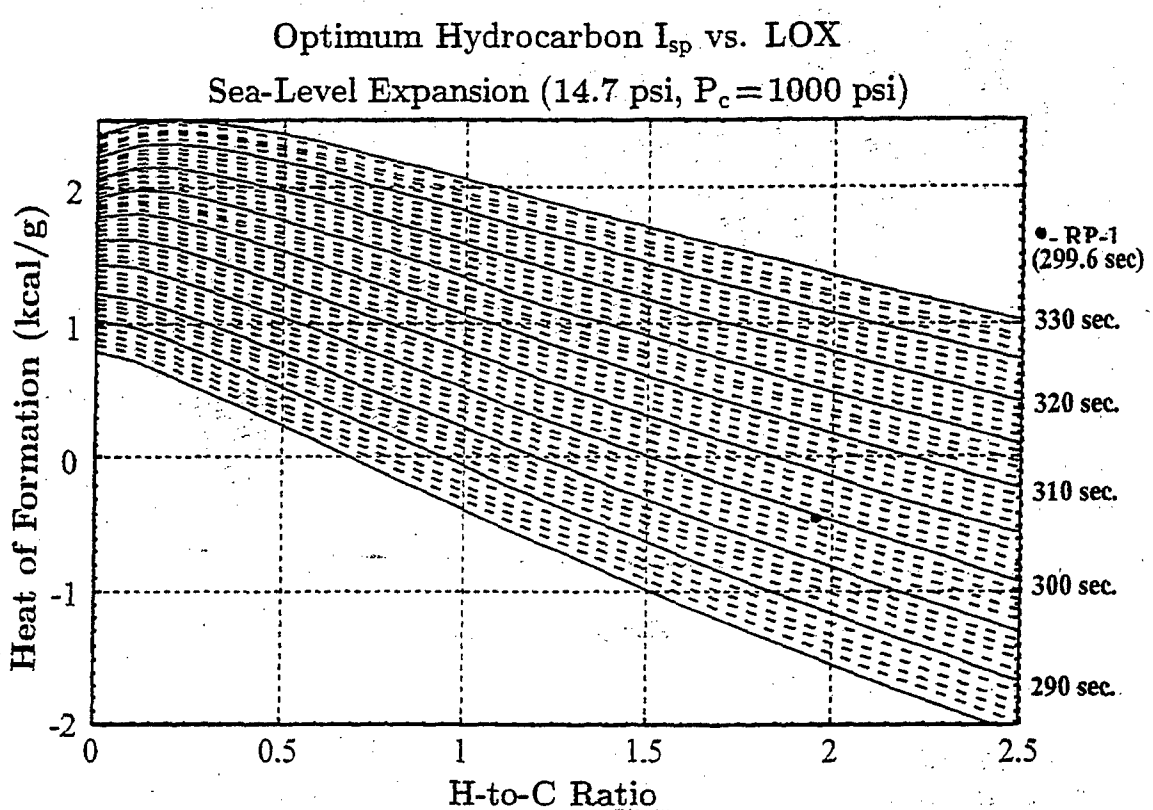

Figure 1–Sea-level specific impulse for hydrocarbon fuels optimized against liquid oxygen. The ambient and chamber pressures are given in the title. Solid lines separate five-second intervals and dashed lines denote single-second contours. The filled solid circle represents RP-1.

A number of important general trends are immediately apparent. The trade between high energy and high hydrogen content, although perhaps appreciated on a qualitative basis, is here put on a firm quantitative foundation. In fact, by calculating the slope of each of the iso-I_{sp} lines it can be plotted, as in Figure 3 for sea-level expansion. It is to be noted that around RP-1, an increase in the heat of formation of one kcal/gram has roughly the same performance impact as a unit increase in the molar hydrogen-to-carbon ratio. As the search for new hydrocarbon rocket fuels is conducted among high energy molecules unsaturated either by virtue of rings or multiple bonds, the countervailing penalty associated with loss of hydrogen must be appreciated. Ideally new fuel development should focus on, to the greatest extent allowed by the constraints of chemical valence, those regions of the performance space perpendicular to the iso-I_{sp} lines. Conversely, to the extent that enthalpy-enhancing chemical transformations move a fuel parallel to an isoperformance contour, the effort going into that reaction can be considered to have been wasted. Even worse, although fuel sensitivity and stability are known to depend in a rather complicated way upon a number of intra molecular, intermolecular, and environmental conditions, extra molecular energy will tend to undermine fuel storability and safety. The hydrogen-content/enthalpy trade-off, along with the powerful constraint imposed by chemical valence, serve to at least partially justify the current, if otherwise seemingly primitive, choices of long standing.

For a given value of the specific impulse the optimum oxidizer-to-fuel ratio is similarly determined by only the fuel's enthalpy content and atomic composition. This is shown for each of the sea-level iso-I_{sp} lines of Figure 1 in Figure 4. (It should be noted that the additional dependence upon the heat of formation, already displayed in Figure 1, has been suppressed.) The significant deviations from stoichiometric combustion

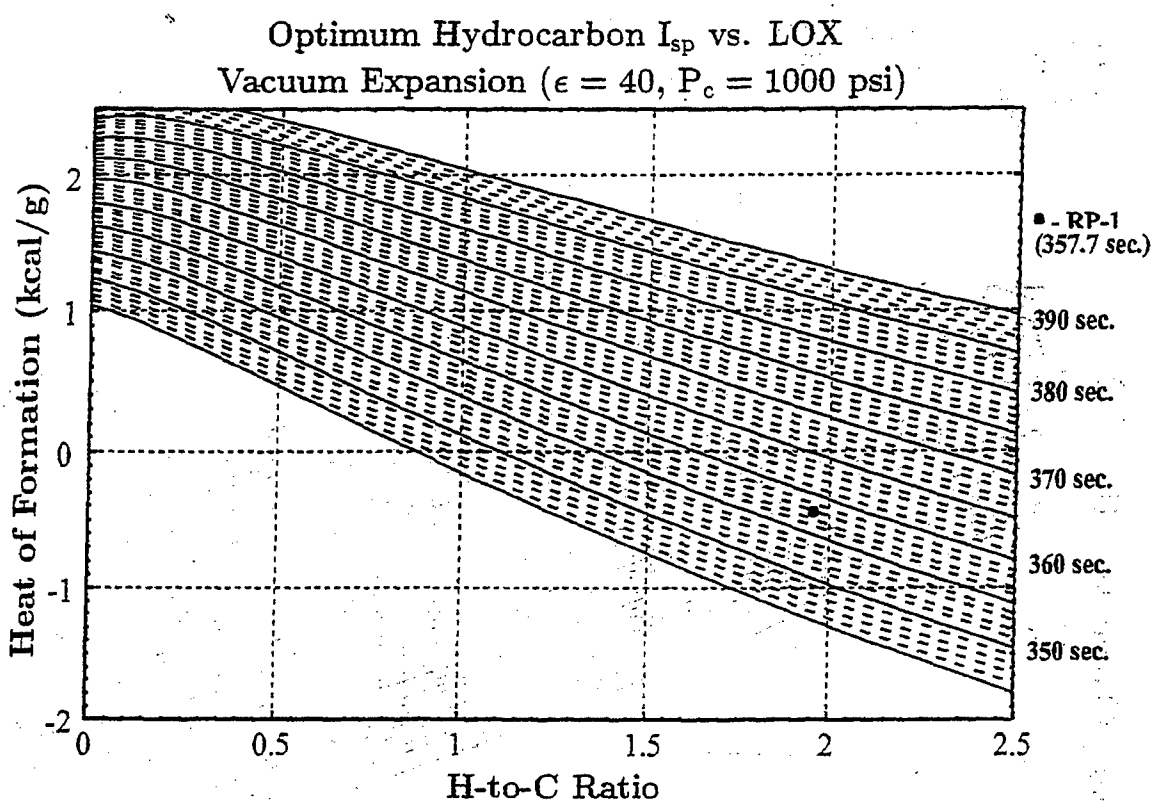

Figure 2–Vacuum specific impulse displayed as in the previous figure but for the indicated expansion ratio and chamber pressure.

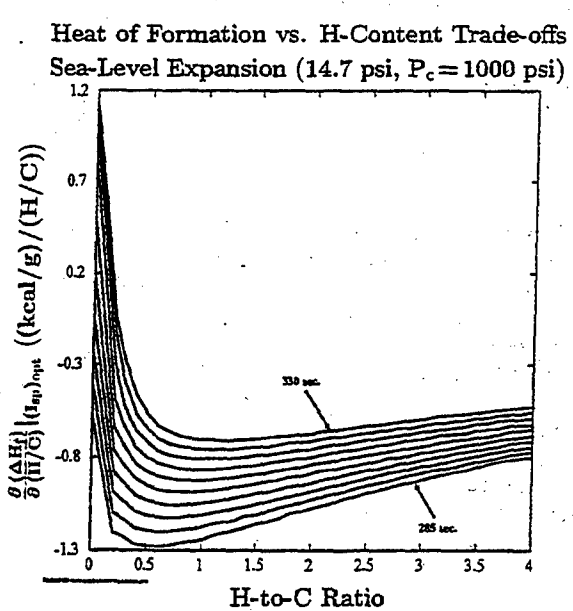

Figure 3–The tradeoff between heat of formation and hydrogen content for sea-level conditions as defined by the slope of the five-second iso-I_{sp} lines of Figure 1.

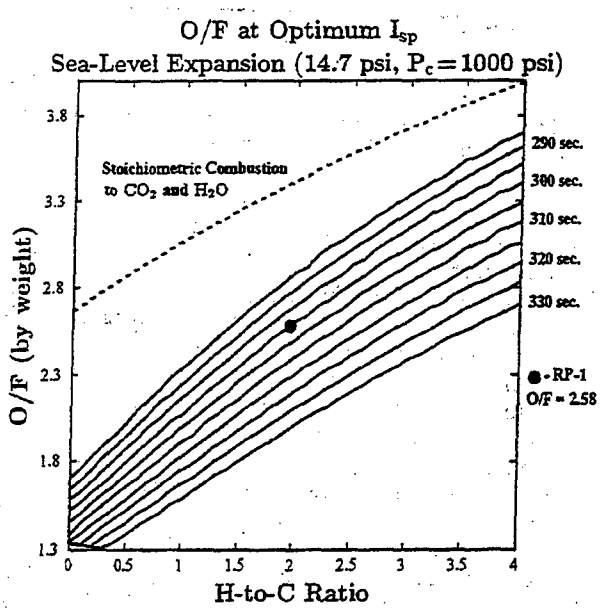

Figure 4–The optimum mixture ratio for the five-second sea-level specific-impulse contours of Figure 1. The dashed line is that which would result from full stoichiometric oxidation of the carbon and hydrogen.

to carbon dioxide and water illustrate the fundamental differences between standard-state combustion and combustion in an optimized, rocket engine due to the performance advantages of low-molecular-weight ejecta.

Although not displayed here, a number of other useful, quantitative trade-offs can be derived from the information in Figures 1 and 2. The gradient of the specific impulse at any point defines those relative changes in the independent parameters which yield the maximum performance increase. Also, the divergence of the specific impulse would quantify the sensitivity of performance to uncertainties in the independent parameters.

Specific Impulse of Hydrocarbon-Fuel Families

Using Figure 1 (or 2) as a template, the I_{sp} of related fuels can be compared on a common basis and performance trends for the given conditions can be insightfully justified. Thus, the intrinsic possibilities and limitations of the functional groups and chemical transformations represented by such a family can be elucidated. The heats of formation for the molecules in this section come from the published literature[7] or the author's notes.

The two most common ways of increasing the enthalpy content of a fuel molecule: formation of double bonds and cyclization, are represented in Figures 5 and 6. Superimposed on a portion of the sea-level reference grid of Figure 1, Figure 5 contains a pair of lines which fully characterize the specific impulse of the linear alkanes and the linear terminal alkenes. The alkenes all lie along a vertical line reflective of their common C_nH_{2n} molecular formula. The positions of specific molecules are denoted by an X along with the total number of carbon atoms. Each family's trend with increasing number of carbons toward the position of RP-1 should be noted along with the general inclination of the family with respect to the iso-I_{sp} lines. The open circles represent the position of the indicated Benson-type,[8] additivity groups[9] considered in isolation. The location of a molecular fuel in the performance space can then be seen as an appropriately normalized combination of its composite Benson-type groups. A similar plot is presented as Figure 6 for rings containing only single bonds and those with a single double bond. Note here that the specific-impulse effects of hydrogen loss almost exactly balances the enthalpy gain of the double bond in going from cyclohexane to cyclohexene.

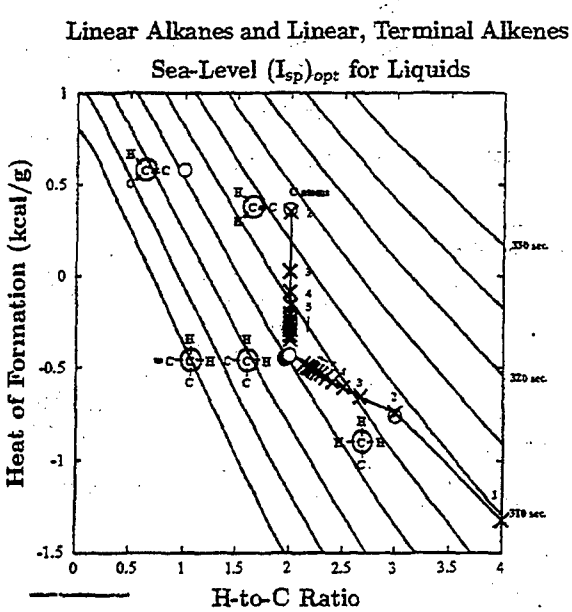

Figure 5–Sea-level specific impulse for the linear alkane (bent line) and linear terminal alkene (vertical line) families. See the text for more detailed discussion.

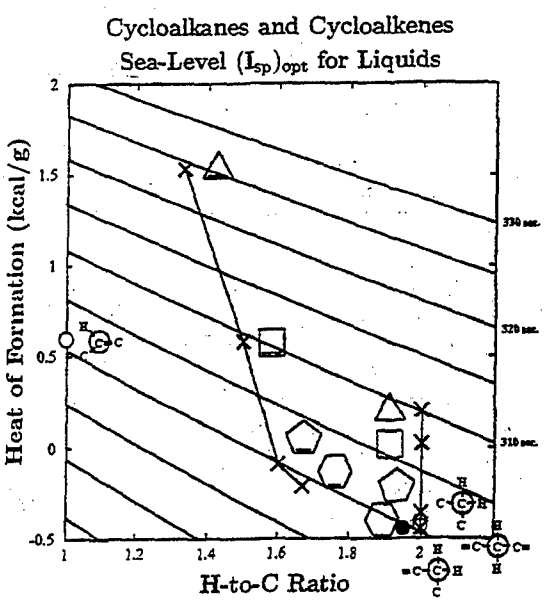

Figure 6–Sea-level specific impulse for rings containing only single bonds and those containing one double bond.

[7] J.B. Pedley, *Thermochemical Data and Structures of Organic Compounds*, Vol. I, (Thermodyn. Research Cent., College Station, TX, 1994).

[8] S.W. Benson, *Thermochemical Kinetics*, Second Ed., (Wiley, New York, 1976).

[9] N. Cohen, *J. Phys. Chem. Ref. Data*, 25, 1411 (1996).

A number of strained-cage compounds are presented in Figures 7 and 8. Beginning at the lower right of Figure 7, hydrogen can be removed and energy can be added to the norbornane cage either by forming three-membered rings to ultimately produce quadricyclane at the top of the plot or by forming double bonds, leading eventually to norbornadiene at the far left. The extent to which relatively little of the added energy is manifested as extra specific impulse is especially striking. Figure 8 describes a number of prismanes, which, being polymers of CH all lie along a vertical line at unity H-to-C ratio. Except for tetrahedrane at the top, the remainder can be thought of as being formed from a band or ribbon of the indicated number of four-membered rings joined at their edges. The striking reversal of the family with number of cyclobutane faces can be attributed to the initial reduction and subsequent increase of strain associated with passing through carbon bond angles more nearly tetrahedral as the ribbon grows in size.

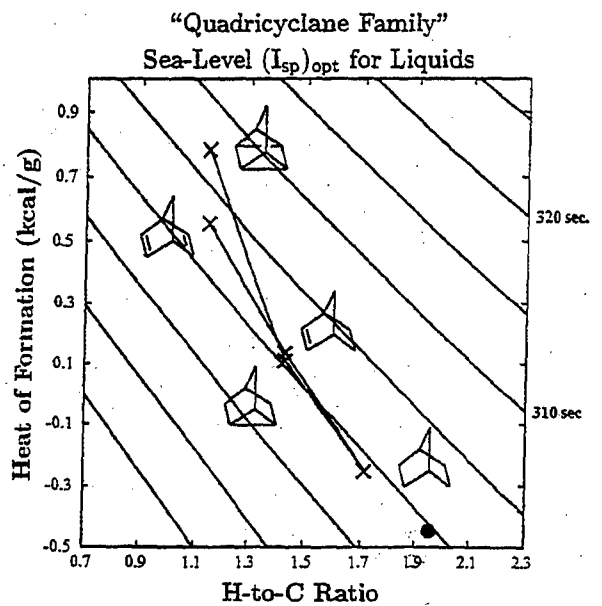

Figure 7–Sea-level specific impulse of molecules including quadricyclane which result from dehydrogenation of norbornane through cyclization or the formation of double bonds.

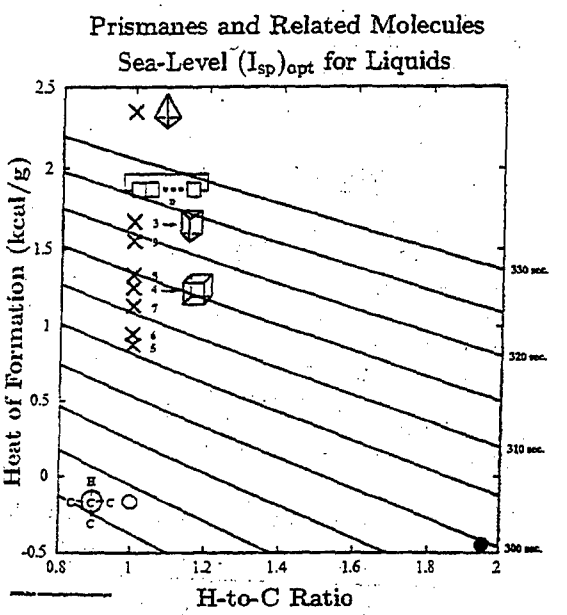

Figure 8–Sea-level specific impulse of a number of prismanes. See the text for a description of the notation.

① - add a period to be consistent

Figure 9 describes a number of molecules related to bicyclopropylidene, a fuel under active development by the Propellants Branch at AFRL and marked "3,3" in the figure. Referred to as the "bow-tie" family, these molecules are interconverted through changing the indicated size of saturated rings at either end of a double bond. A number of compounds in which saturated rings are connected by spiro linkages, instead, are displayed in Figure 10. The unconnected points indicate bicyclic systems in which the two rings have the indicated sizes. The connected points represent the polymers formed by the repeated joining of either three- or four-membered rings in linear chains. The declining specific impulse with increasing energy and chain length in the four-membered-ring polymer should be noted. Although its specific impulse change with chain length may not be especially encouraging, the three-membered ring family might be especially suitable in circumstances requiring an easily blendable fuel of tunable physical properties.

Simple Mission Performance Metrics Involving Specific Impulse

While specific impulse constitutes the most fundamental and commonly used measure of propellant performance, an approximate relationship between I_{sp} and more concrete mission parameters might be useful in gauging the real impact of a proposed new fuel. This is also motivated by the recognition that as reflected in the simple, single-stage rocket equation:

$$\frac{M_{pl}}{M_{tot}} = e^{-\Delta v/g_o.I_{sp}} \qquad (1)$$

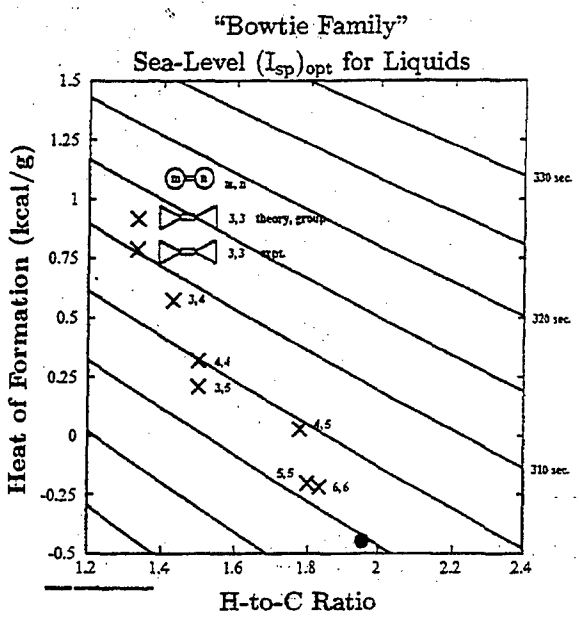

Figure 9–Sea-level specific impulse of the "bow-tie" molecules. See the text for a description of the notation. The two positions given for bicyclopropylidene (3,3) denote somewhat divergent experimental and theoretical heats of formation.

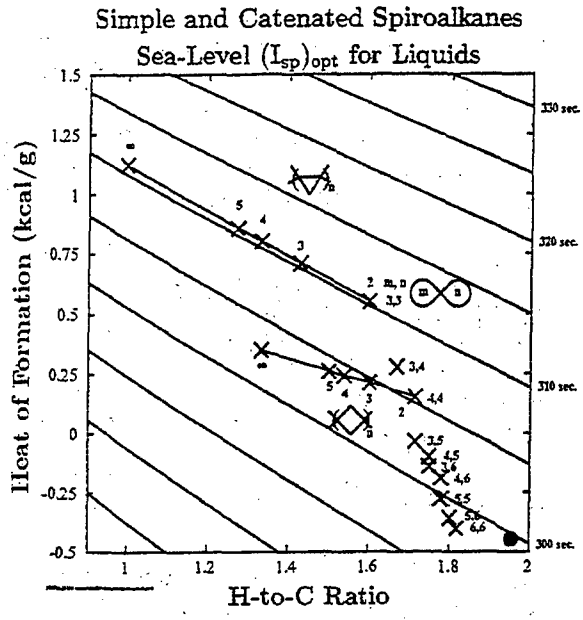

Figure 10–Sea-level specific impulse of the bicyclic spiroalkane family and two spiroalkane polymers. See the text for a description of the notation.

the exponential dependence upon I_{sp} can lead to a situation in which relatively small improvements in specific impulse produce larger effects in terms of payload mass or gross lift-off mass, and that because of this, propellant combinations which seem only modestly improved might be discounted unnecessarily.

By taking the derivative of either the payload mass or the total initial mass with respect to specific impulse with the other parameters held constant and upon linearizing for small changes, one obtains:

$$\frac{\Delta M_{pl}}{M_{tot}} = -\frac{\Delta M_{tot}}{M_{tot}} = \frac{M_{tot}}{M_{pl}}\left[\frac{\Delta v}{g_o I_{sp}}\, e^{-\Delta v/g_o I_{sp}}\right]\frac{\Delta I_{sp}}{I_{sp}} = k\,\frac{\Delta I_{sp}}{I_{sp}} \qquad (2)$$

where the results of the discussion to follow will be expressed in the second, simplified form. This admittedly already approximate relation could be employed as a rough metric for mission masses in the following two ways.

First of all, without reference to any particular vehicle, if one specifies a propellant combination and a mission-dependent velocity change, then the quantity in square brackets in the first form of eqn. (2) can be calculated. For the optimized I_{sp} for liquid-oxygen/RP-1 under the vacuum conditions most typical for a single-stage mission (358.1s) and an effective $\Delta v \approx 9000$m/s for transit to low-earth orbit, the factor in square brackets is around 0.2. That, coupled with an assumption of inverse burn-out mass fraction between 20 and 40, would imply that a single percent increase in I_{sp} might lead to a 4% to 8% increase in delivered mass or an identical decrease in gross lift-off mass.

Alternatively, eqn. (2) could be approximately interpreted in a vehicle-dependent manner. The factor in square brackets could be set using the initial and final masses for the first stage of a real system and equation (1) above. For example, lumping the first stage and a half of the Atlas vehicle[10] into an effective single first stage leads to a value for k in the second form of eqn. (2) of almost 2 instead of the 4 to 8 determined previously. As this accounts for only the first stage of a multistage vehicle and improvements to upper stages generally have a greater impact, this difference in such a crude heuristics is not hardly surprising.

[10] S.J. Isakowitz, *International Reference Guide to Space Launch Systems*, Second Ed., (Amer. Inst. Aeronat. Astronaut., Washington DC, 1991).

These relatively simple-minded metrics can be compared with genuine system analyses. One study conducted by NASA researchers approximately twenty years ago[11] concluded that the relative reduction in the gross lift-off mass of a single-stage-to-orbit-vehicle with fixed payload mass and powered by a hydrocarbon/liquid-oxygen propellant would be approximately 2.4 times (*c.f.* the first term in equation (4)) the relative increase in specific impulse. Results of studies[12] conducted by engineers at Air Force Research Laboratory and making use of conservative engineering assumptions including the constraints of fixed thrust, constant total volume, and no re-optimization of mixture ratio for a proposed drop-in hydrocarbon replacement fuel seem to show the same trends. The first phase of these studies considered the effects on total payload mass of specific impulse in isolation. After averaging over vehicle versions/configurations and missions and reducing the results to the form of eqn. (2), the relative payload increases with each unit increase in relative specific impulse are given by 2.5, 1.5, and 5.5 for the Atlas IIAR, Delta III, and Zenit vehicle families, respectively (*c.f.* the first terms in eqn. (5)). Not surprisingly, Zenit, the vehicle with the most hydrocarbon stages and those that extend later into the sequence is most benefited by replacement with a higher specific impulse fuel. That these values are somewhat less than those roughly estimated from simple manipulation of the rocket equation should not be surprising given the conservative engineering assumptions involved.

Simple Mission Performance Metrics Including Fuel Density

For some types of rocket missions, there is a conventional understanding[13] that instead of the ordinary specific impulse, a better approximate measure of theoretical propellant performance may be the optimized product of the average specific gravity of the composite propellant. D_{prop}, raised to a fixed power and the specific impulse, as:

$$\left[D_{prop}^{a} I_{sp}\right]_{opt} \tag{3}$$

where the density exponent, a, decreases with altitude. Thus, while ordinary specific impulse might be appropriate for interplanetary missions, exponents of approximately one-third and two-thirds are sometimes associated with orbit transfer and boost, respectively. Also, the density specific impulse,[14] the simple product of mean propellant specific gravity and I_{sp}, is also sometimes used as a reference metric. In the following discussion, most of these measures, to the extent that they are construed to directly reflect propellant performance, will be shown to overemphasize the effect of density for the types of missions considered herein.

The NASA study previously mentioned[15] also examined the effects of the density of the fuel itself (in distinction to the mean propellant density used in the preceding paragraph) and concluded that the reduction of gross lift-off mass is given by:

$$-\frac{\Delta M_{tot}}{M_{tot}} = 2.4\,\frac{\Delta I_{sp}}{I_{sp}} + 0.1\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}} \tag{4}$$

where the I_{sp} dependence already discussed is included for comparison. In that study, it was also determined that, at least for the SSTO mission, a density exponent on the mean propellant specific gravity in the conventional form (*i.e.* a in eqn. (3)) of 1/3, although not grossly in error, may somewhat overstate the performance impact of density. After investigating I_{sp} impacts by themselves, the systems analyses performed at AFRL were also conducted in such a way as to include the effects of both density and specific impulse. When these results are averaged as described above and the additional effects due to density change are isolated, the analogous forms of the previous equation become:

$$\begin{aligned}
\text{Atlas IIAR:}\ & \frac{\Delta M_{pl}}{M_{tot}} = 2.5\,\frac{\Delta I_{sp}}{I_{sp}} + 0.25\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}} \\
\text{Delta III:}\ & \frac{\Delta M_{pl}}{M_{tot}} = 1.5\,\frac{\Delta I_{sp}}{I_{sp}} + 0.07\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}} \\
\text{Zenit:}\ & \frac{\Delta M_{pl}}{M_{tot}} = 5.5\,\frac{\Delta I_{sp}}{I_{sp}} + 0.32\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}}
\end{aligned} \tag{5}$$

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[11] J.W. Frankenfeld, *et al.*, *op. cit.*, p. 56, but also see J.J. Notardonato, P.A. Masters, *op. cit.*

[12] R. Nichols, *personal communication.*

[13] See, *e.g.*, J. Friedman and I.A. Kanarek, "Evaluation of the Relative Importance of Specific Thrust and Propellant Density for Rocket-Boosted Missles," *Technical Report*, North Amer. Aviation Aerophys. Lab., No. AL-986, Jan. 20, 1950, R.S. Kraemer, in *Handbook of Astronautical Engineering*, edited by H.H. Koelle, (McGraw-Hill,New York,1961), p. 20-12, J.N. Wilson, *loc. cit.*, J.J. Notardonato, P.A. Masters, *op. cit.*, D.C. Rapp, *op. cit.*, J.W. Frankenfeld, *et al.*, *loc. cit.*

[14] G.P. Sutton, *op. cit.*, pp. 246-247.

[15] J.W. Frankenfeld, *et al.*, *loc. cit.* and J.J. Notardonato, P.A. Masters, *op. cit.*

for each of the indicated systems. It thus appears that for both conservatively altered systems and wholly redesigned vehicles, the density of the fuel itself may be roughly 10 to 25 times less important than the specific impulse. The interests of comparing and extending these simple heuristics to other propellant characteristics may be served by additional studies currently being conducted at Air Force Research Laboratory which may also address the variation of long-term costs and other important operational parameters with propellant properties.

Finally, the preceding metrics linear in the specific impulse and fuel density can be compared with the conventional measures defined by eqn. (3). Of the fractional density exponents considered above, 1/3 comes the closest to reproducing the results of all three AFRL systems analyses, which, it should be recalled, involved vehicles with only first-state improvements, as well as those with multistage improvements.

A Comparison of RP-1 and RG-1

The preceding considerations can be insightfully applied to the differences between the standard rocket kerosenes of American (RP-1) and Russian (RG-1) manufacture. Table 1 contains a number of characteristics of the two fuels averaged over the three independent studies with the differences of RG-1 relative to RP-1 given in the final line. The use of Russian kerosene in this country is sometimes advocated on the basis of the middle three columns of Table 1; namely, it is sometimes argued that RG-1 enjoys a clear density advantage while having the same nominal net heat of combustion. It appears, however, that, at least for these three studies, slight declines in measured heat of formation and measured hydrogen content combine to produce a decline in one-dimensional specific impulse of nearly a second compared to RP-1. Assuming the ten- to twenty-five-fold greater importance of I_{sp} already discussed, it is not obvious that Russian kerosene's density advantage is not accompanied by an off-setting penalty.

Table 1
A Comparison of RP-1 and RG-1 Thermochemistry and Performance

Measured Δh_f (cal/g)	Measured Net Δh_{comb} (BTU/lb)	Specified Net Δh_{comb} (BTU/lb)	Fuel	Measured ρ_{fuel} (g/cm^3, 22°C)	Measured r(H/C)	Sea Level I_{sp} (sec.)
-475	-18640	-18500	RP-1	0.806	2.008	299.8
-508	-18540	-18500	RG-1	0.832	1.991	299.0
-6.9%	-0.53%			+3.2%	-0.85%	-0.27%

It must be admitted that the differences described in Table 1 are rather small (that of the heats of formation amounts to approximately one-half kcal/mol per carbon atom), and so it is possible that there exist unreleased studies which might change this assessment. In addition, more sophisticated systems analyses for particular types of missions or other of its other physical or chemical properties might indicate a clear preference for RG-1 over RP-1. Nevertheless, it appears from the present considerations that at least the common qualitative understanding or justification of the relative advantages of the kerosenes may need to be more carefully examined. Further, the preceding type of analysis would seem to support the addition of atomic composition to those properties covered by the military specification[17] because of its importance in determining performance.

The comparison of RP-1 and RG-1 also provides a context in which to further investigate the relative importance of density and specific impulse. What follows is in the spirit of a proof by contradiction. Performance parameters of the form defined in equation (3) are assumed and then a certain class of them is shown to be inconsistent in a hypothetical case with common sense notions of what it means to have an improved propellant. Consider a thought experiment designed to approximate the effect of jettisonable dead-weight upon the performance of a rocket mission. Suppose that a dense, chemically and physically inert material were mixed with the propellant and that during firing it disappeared at a constant rate. While imparting no momentum

[17] "Propellant, Kerosene," *Military Specification*, No. MIL-P-25576C, 10 Jan. 1967.

thrust to the vehicle or heat to the propellant stream, it could increase the effective density of the propellant. While it would seem odd to characterize this new "propellant combination" as preferable to its additive-free baseline, it is fair to ask whether an improvement in the sort of performance metrics described by equation (3) might nonetheless result. The portion of the specific impulse due to momentum thrust can be described by the familiar expression:

$$I_{sp,\,mom} = \frac{\sqrt{2\Delta h}}{g_o} \tag{6}$$

where Δh is the specific (per mass) enthalpy change between chamber and exhaust. If one further assumes that there is a proportional change in pressure thrust between the propellant with and without additive and that the additive changes neither the optimum mixture ratio for the remainder of the propellant considered in isolation nor the specific enthalpy release of the additiveless portion of the additive-augmented "propellant," algebraic manipulation yields the ratio of the additive-enhanced to baseline performance, as:

$$\frac{[D^a I_{sp}]_{opt+b}}{[D^a I_{sp}]_{opt}} = \frac{\sqrt{1-f_b}}{\left[1 - f_b\left(\frac{D_{prop}}{D_b} - 1\right)\right]^a} \tag{7}$$

where f_b is the mass ratio of inert additive, D_b is its effective specific gravity, and D_{prop} is the mean specific gravity of the additiveless propellant. This ratio is greater than one when the performance metrics defined by eqn. (3) erroneously indicate that a propellant can be improved by the addition of dead weight. In the limit of infinite additive density, this occurs for any additive mass fraction when the density exponent exceeds 1/2. Alternatively, if, for example, the baseline propellant specific gravity is one and the additive specific gravity is eight, than this condition is fulfilled for all $a > 0.57$. Finally, when applied to the comparison of RP-1 and RG-1, eqn. (7) predicts that the performance of RP-1 can not be made to exceed that of RG-1 through the addition of dead weight for $a = 1/3$, but that for 2/3 and 1, 6% and 2% of an additive with specific gravity of eight will allow it to do so. Together with the comment relating linear and nonlinear density-weighted metrics that ends the preceding section, it appears that non-linear performance metrics (eqn. (3)) in which density is weighted with an exponent greater than 1/3 may be overstating the advantages of propellant density and that the often used density I_{sp} almost certainly does so, at least insofar as such heuristics are considered to directly describe propellant performance. While this may not be particularly surprising, it does place understanding of these trends on a rather more firm, quantitative foundation.

SUMMARY AND CONCLUSIONS

Among the hydrocarbon rocket fuels optimum performance generally increases with the specific enthalpy of formation, the hydrogen-to-carbon ratio, and the density. For a specific oxidizer and reference rocket conditions, the first two determine theoretical, one-dimensional specific impulse by themselves and therefore may be used as a grid in which to insightfully map families of candidate molecules and discern their fundamental promise and limitations. It is then, for example, clearly seen how the extra energy imparted by the unsaturation of multiple bonds and strained rings is at least partially offset by the accompanying loss of hydrogen. This may be seen as the source of the respectable performance of the simple refined petroleum currently employed in rocket engines. Further, failure to fully appreciate this tradeoff imposed by the limits of chemical valence seems to be responsible for many of the otherwise surprisingly discouraging results obtained from simple performance calculations of high-energy candidate fuels.

Although, of course, no new propellant combination should be recommended for expensive and time-consuming further testing without sophisticated and exhaustive system studies, simple performance metrics like those outlined here may have value in promoting understanding of the trade-offs involved and allow affordable screening of even immense data bases of prospective molecules. Herein, single percent improvements in specific impulse alone have been approximately associated with payload-mass-fraction increases or gross-lift-off-mass reductions of approximately two to ten percent, depending on the engineering assumptions obtaining. Further, it appears that the relative effects of density on mission masses may be between ten and twenty-five times smaller than those of I_{sp} and that the product of density raised to the 1/3 power and specific impulse may provide a simple metric to encapsulate these effects; higher density exponent can be shown to be contra-indicated by a lack of internal consistency in their assumptions. Finally, these simple, approximate performance metrics are unable to advance Russian rocket kerosene as preferable to the American version, but do seem to indicate a need for hydrogen content to be included in the military specification for hydrocarbon rocket fuels.

In the future it is hoped to extend this work by applying these sorts of simple metrics to large data bases of hydrocarbon molecules in an effort to approximately rank fuels according to their mission-specific utility. Clearly more work needs to be done to further characterize and specify these and related simple metrics and the author is especially interested in learning of any other, similar results.

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SYMBOLS

a	Exponent used to weight specific gravity in density-weighted performance metrics (see eqn. (3))
D_{prop}	Mean propellant (oxidizer plus fuel) specific gravity
D_b	Effective specific gravity of hypothetical dead weight
Δv	Mission-specific velocity increment
Δh	Specific (per gram) enthalpy change between chamber and exhaust
Δh_f	Specific (per gram) ethalpy of formation
Δh_{comb}	Specific (per gram) enthalpy of combustion
ϵ	Nozzle expansion ratio used to define vacuum specific impulse
f_b	Mass fraction of hypothetical dead weight
g_o	Sea-level gravitational acceleration
I_{sp}	Specific impulse
$I_{sp,mom}$	The portion of specific impulse due to momentum thrust alone
$(I_{sp})_{opt}$	Specific impulse optimized for mixture ratio
$\left[D_{prop}^a I_{sp}\right]_{opt}$	Optimized density-weighted performance metric
$\left[D_{prop}^a I_{sp}\right]_{opt+b}$	Same as previous but including hypothetical dead weight
k	Multiplier of relative specific-impulse changes on changes in mission masses
LOX	Liquid oxygen
M_{pl}	Payload mass
M_{tot}	Gross lift-off mass
P_c	Chamber pressure
ρ_{fuel}	Density of the fuel alone
r(H/C)	Molar hydrogen to carbon ratio
RP-1	American rocket kerosene
RG-1	Russian rocket kerosene

Hydrocarbon Fuels Optimization

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AFRL/PRSP
Air Force Research Laboratory
Space and Missle Propulsion Division
Propellants Branch

Outline

- Introduction and Motivation
- Web-Based, Graphical Interface to CEA
- Specific Impulse of Families of Hydrocarbon Rocket Fuels
- Mission-Performance Metrics Involving Specific Impulse
- Including Density in Performance Metrics
- Conclusions and Future Directions
- Acknowledgments

Introduction and Motivation

- Screen Exotic, High-Energy Hydrocarbon Rocket Fuels
- Devise Simple, Mission-Specific Performance Metrics
- Understand Hydrocarbon Fuels "As a Class"
- Justify Current Fuels

Interface to ODE Code

- **Front End to CEA**
  NASA-McBride and Gordon
  www.grc.nasa.gov/www/CEAWeb
- **User's Browser Connects to Linux Web Server**
- **Inclusion of SQL-Compliant Data Base**

Interface to ODE Code

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Density-Weighted Specific Impulse Optimized vs. Several Oxidizers

RP-1
$CH_{1.952}$

Sea-level (P_c=1000.0 psi, P_e=14.7 psi with Equilibrium Flow):

Oxidizer	Opt'd $D^{2/3}I_{sp}$(sec.)	O/F (by wt.)	T_{chamb} (K)	$D_{prop.}$ (spec. grav.)	I_{sp} (sec.)
LOX	305.1	2.69	3691	1.028	299.6
N_2F_4	351.1	3.66	3840	1.277	298.3
N_2O_4	320.5	4.38	3471	1.249	276.3
98% H_2O_2	329.1	7.26	2945	1.308	275.1
90% H_2O_2	313.5	7.89	2780	1.281	265.8
IRFNA	313.2	5.22	3140	1.301	262.9
HAN	332.8	11.56	2704	1.545	249.1

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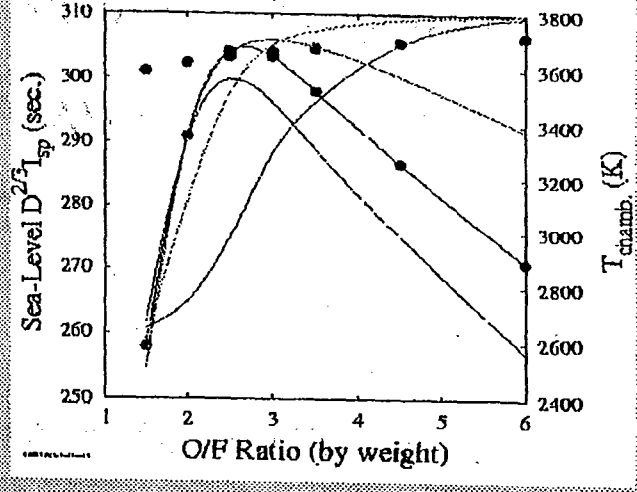
Plot of Performance Parameters vs. Mixture Ratio

One-D Rocket Characteristics vs. Mixture Ratio
$CH_{1.952}$ vs. LOX



I_{sp} of Hydrocarbon Families

Specific Impulse for One-Dimensional, Adiabatic, Equilibrated, Isentropic Expansion Optimized vs. LOX

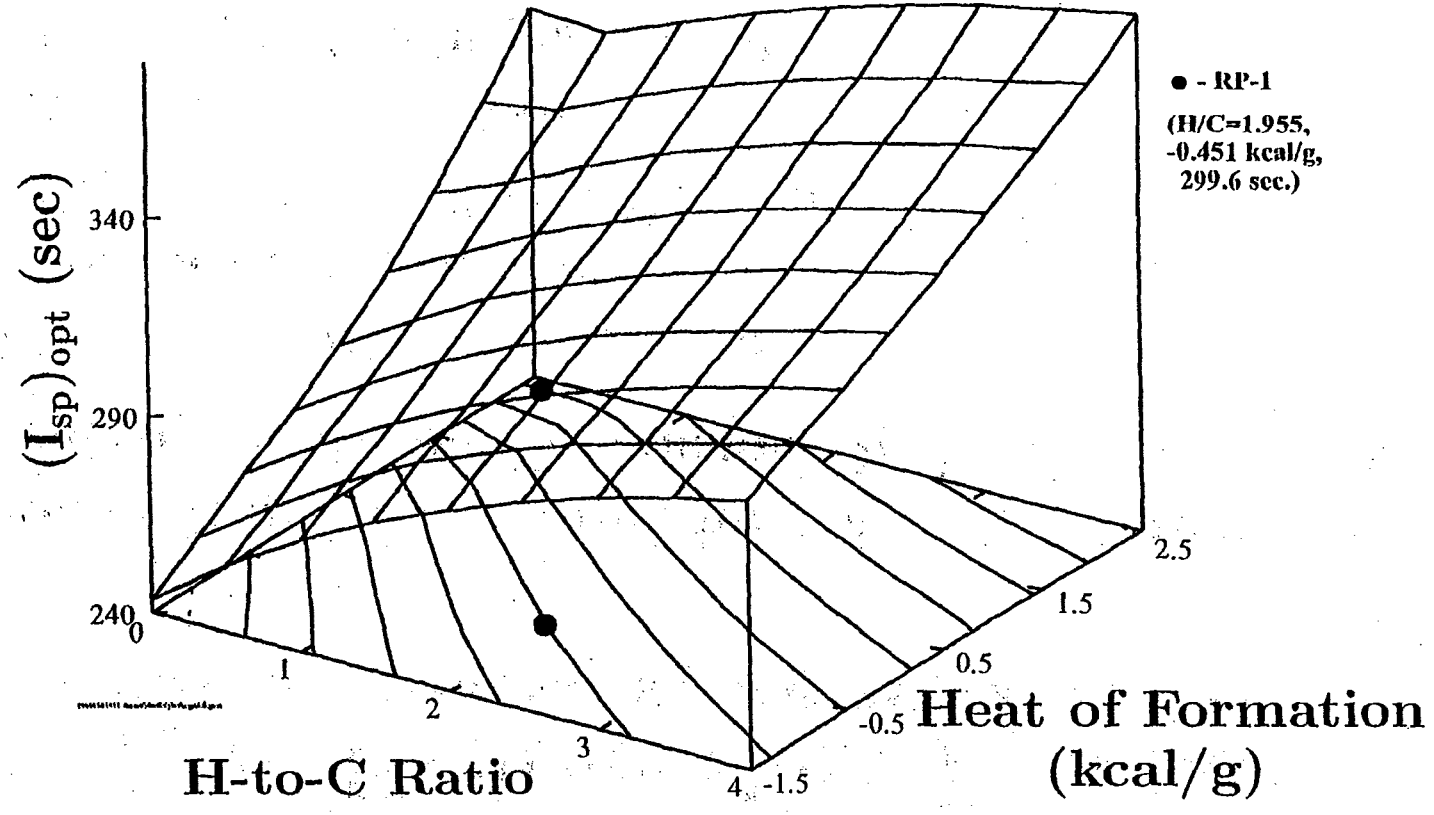
Reference Rocket Conditions:

- **Sea-Level Expansion**
  $P_{chamber} = 1000$ psi, $P_{exhaust} = 14.7$ psi
- **Vacuum Expansion**
  $P_{chamber} = 1000$ psi, $\epsilon = 40$

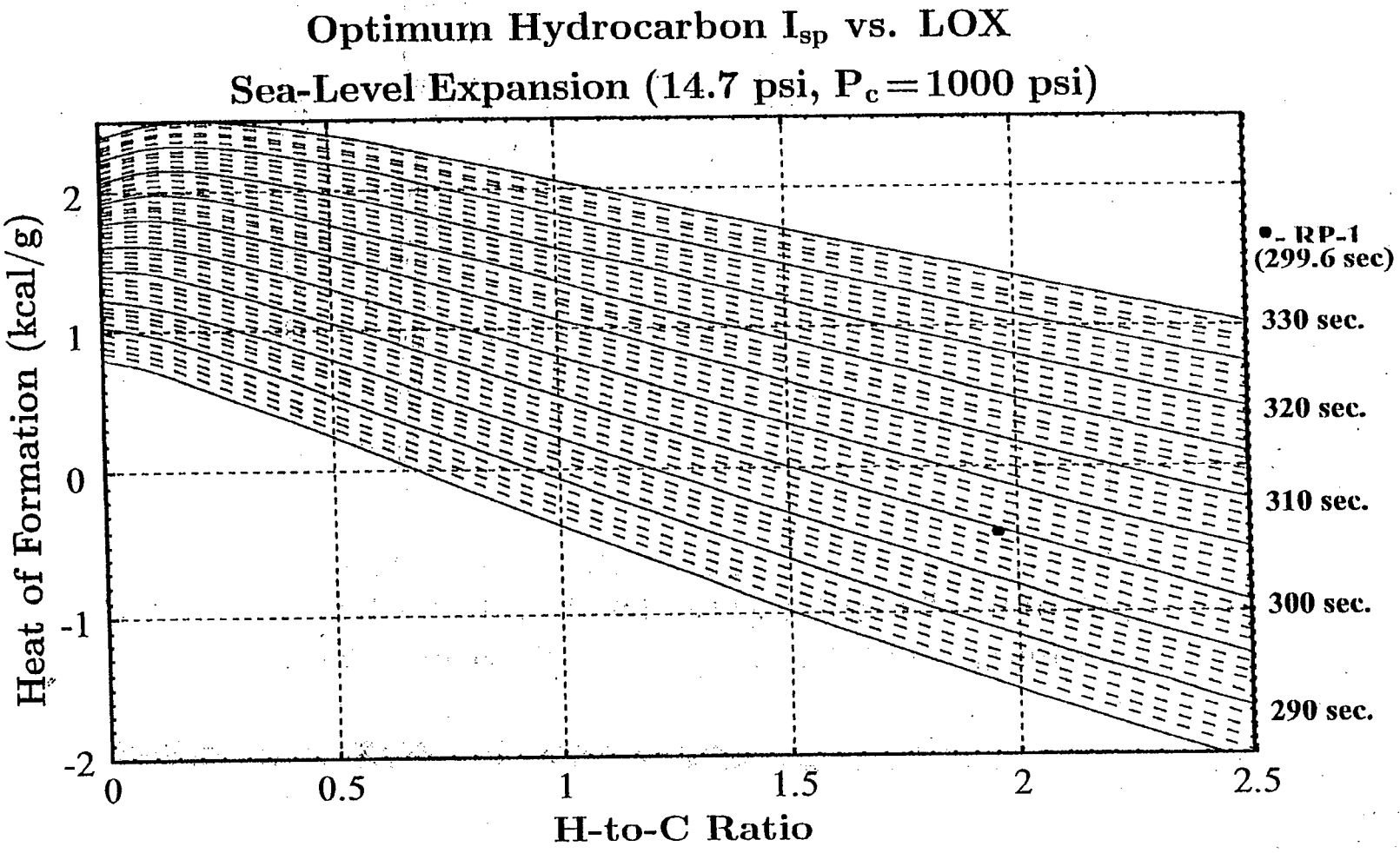
$\Rightarrow (I_{sp})_{opt}$ **is determined by** Δh_f **and** $r(H/C)$ **alone**

Parameter Space

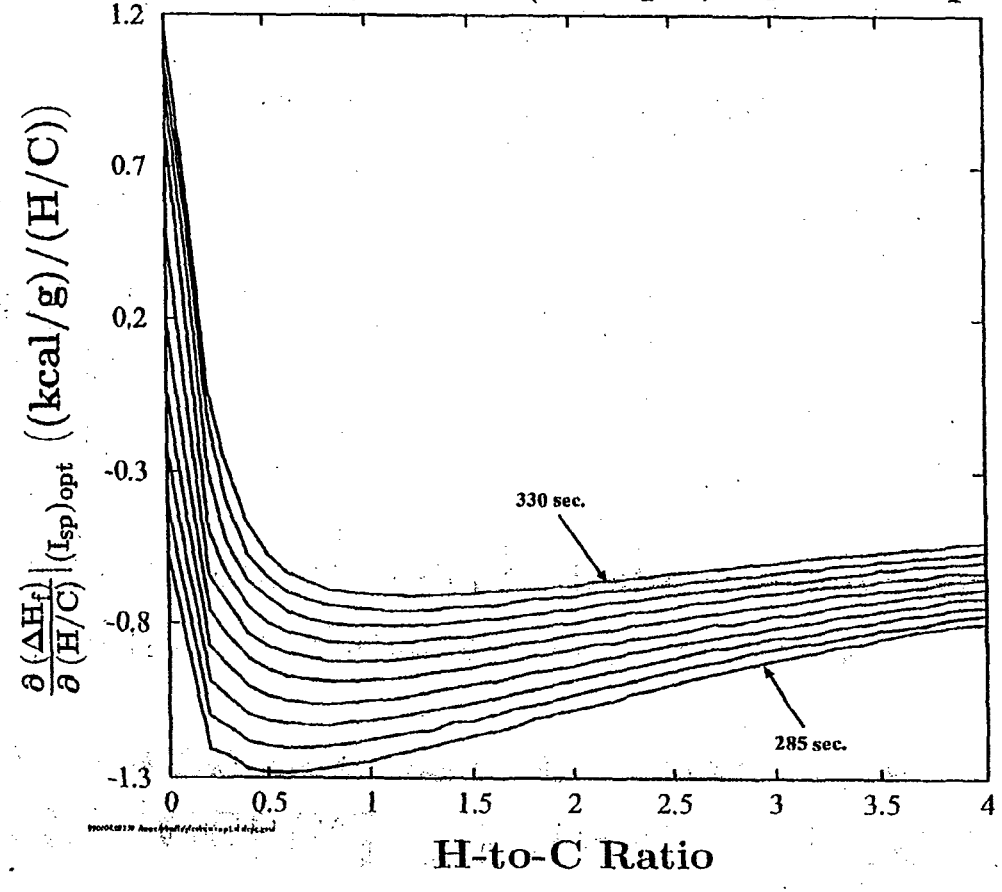
Optimum Hydrocarbon I_{sp} vs. LOX
Sea-Level Expansion (14.7 psi, $P_c = 1000$ psi)

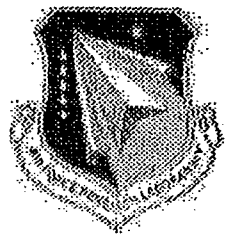


Projected "Iso-I_{sp}" Lines

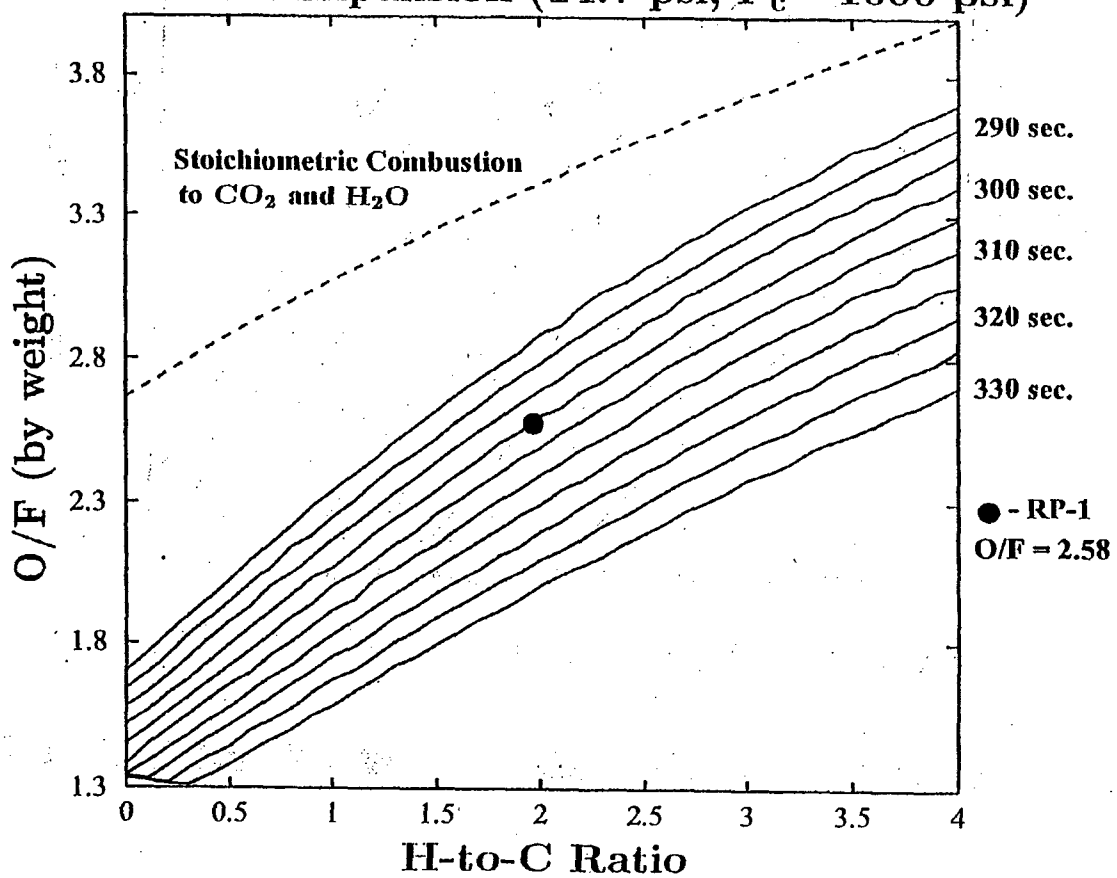


Heat of Formation vs. H-Content Trade-offs
Sea-Level Expansion (14.7 psi, $P_c = 1000$ psi)



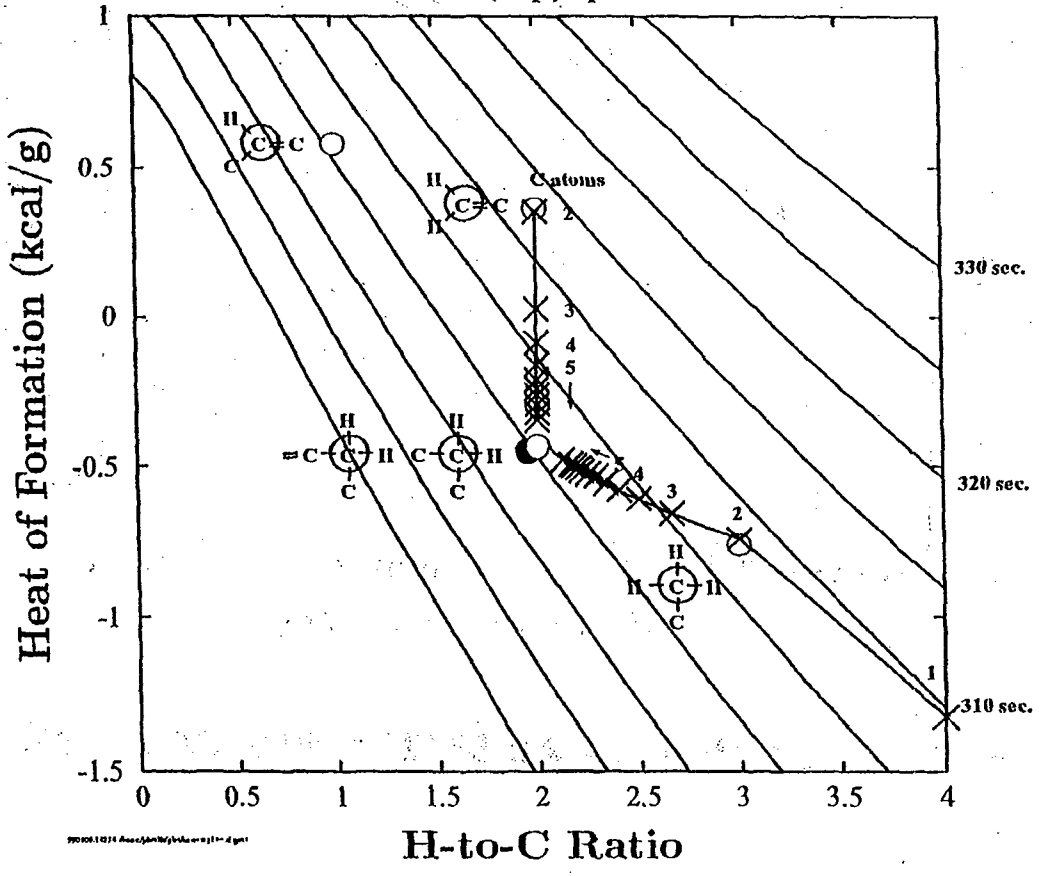


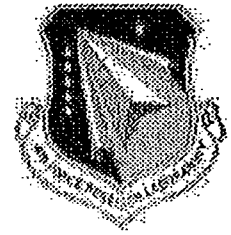
O/F at Optimum I_{sp}
Sea-Level Expansion (14.7 psi, $P_c = 1000$ psi)



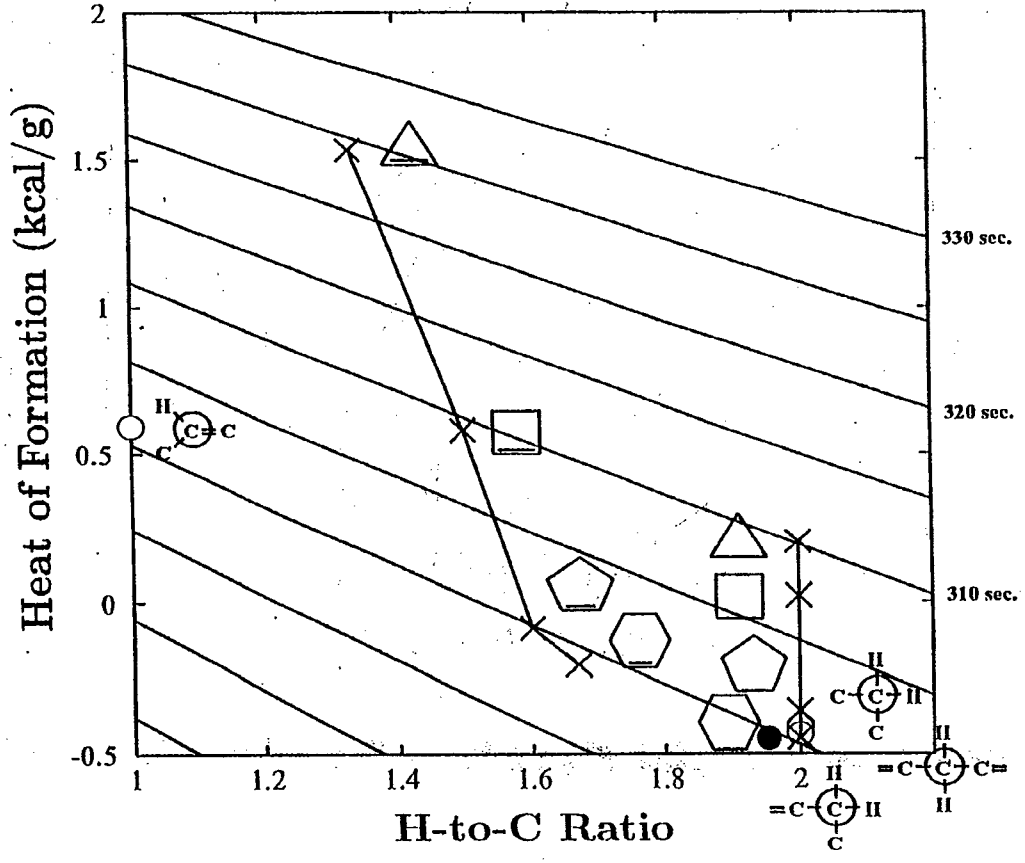
Linear Alkanes and Linear, Terminal Alkenes

Sea-Level $(I_{sp})_{opt}$ for Liquids

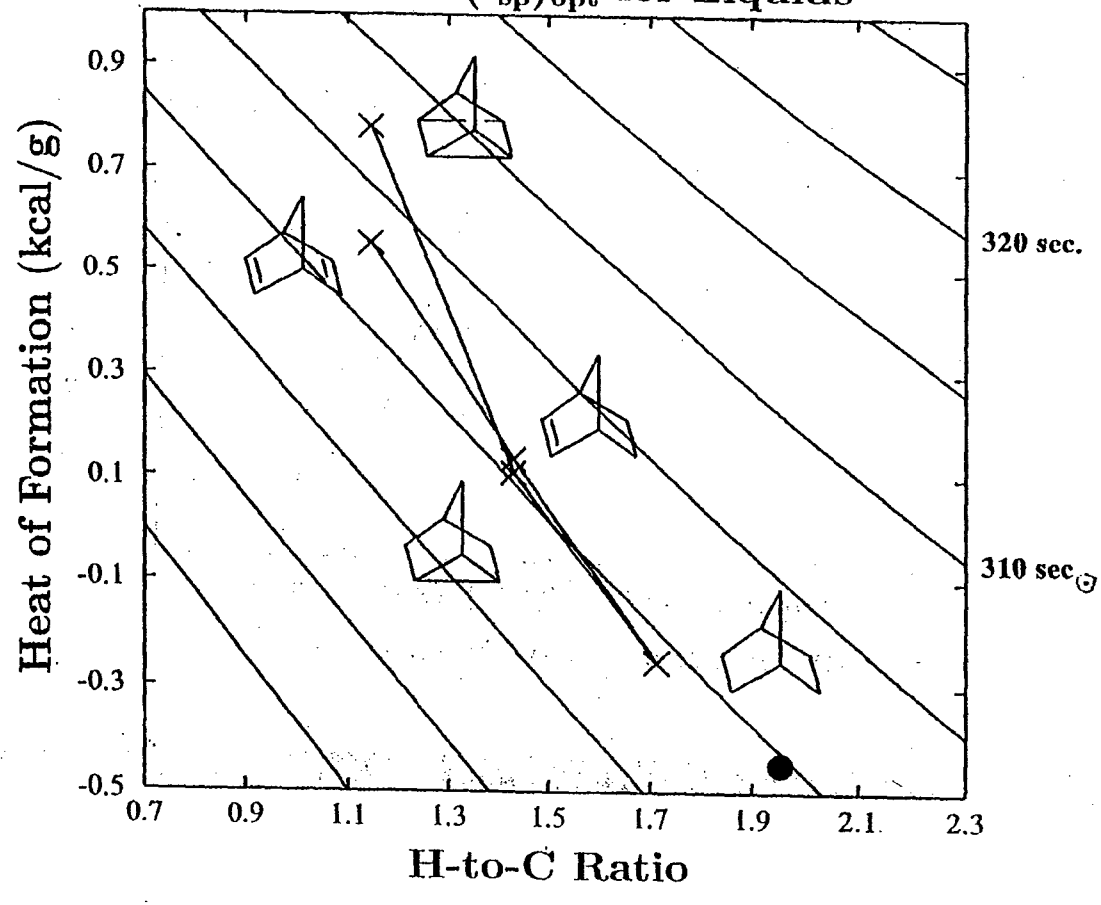




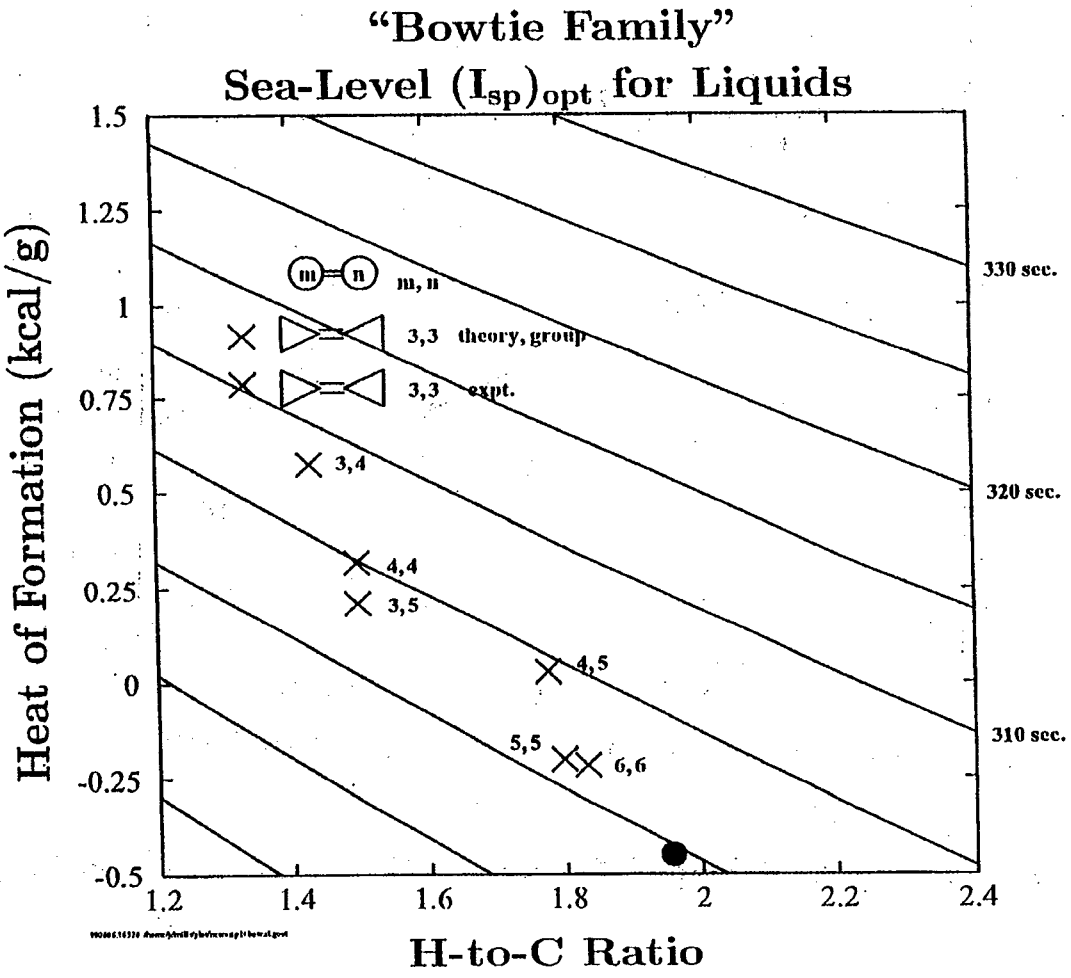
Cycloalkanes and Cycloalkenes
Sea-Level $(I_{sp})_{opt}$ for Liquids

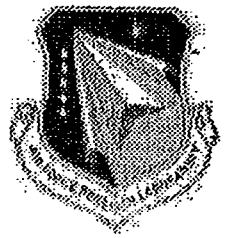


"Quadricyclane Family"
Sea-Level $(I_{sp})_{opt}$ for Liquids

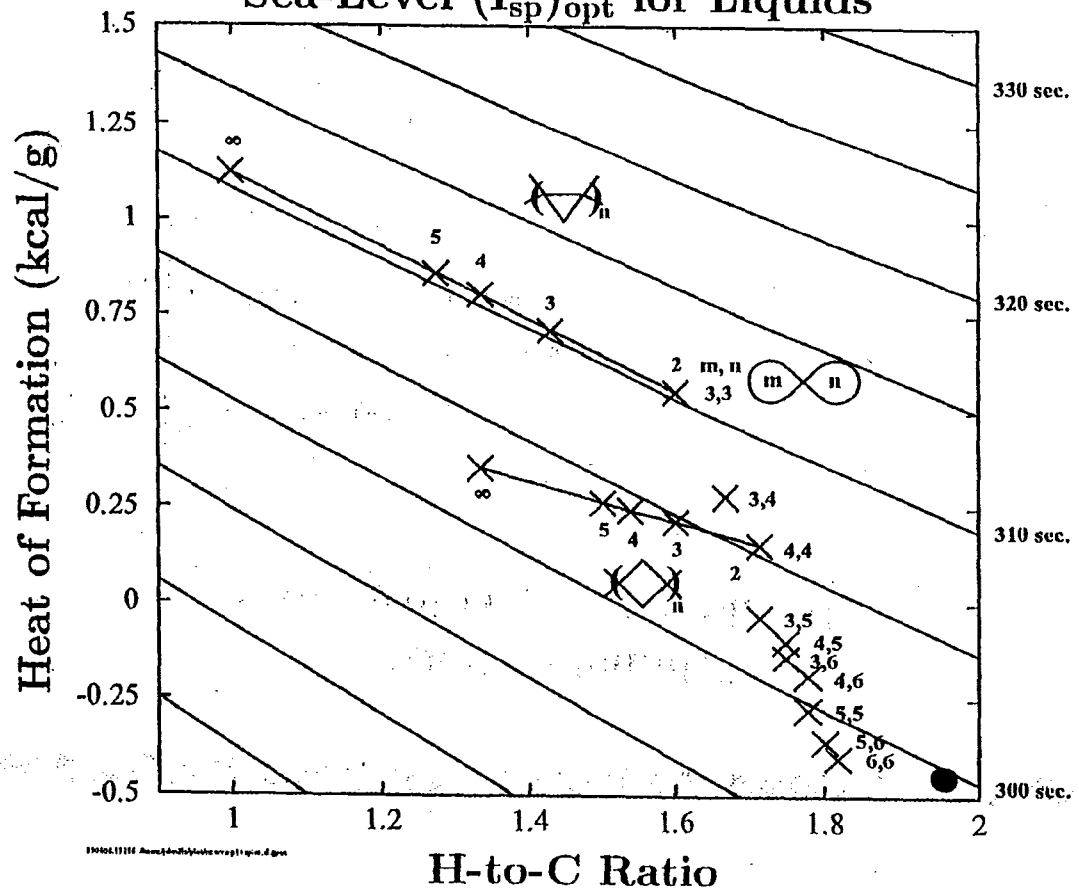


- if you have time, add a period to the end of "sec" for consistency


"Bowtie Family"
Sea-Level $(I_{sp})_{opt}$ for Liquids
Heat of Formation (kcal/g)
H-to-C Ratio
1.5
1.25
1
0.75
0.5
0.25
0
-0.25
-0.5
1.2
1.4
1.6
1.8
2
2.2
2.4
330 sec.
320 sec.
310 sec.
m, n
3,3 theory, group
3,3 expt.
3,4
4,4
3,5
4,5
5,5
6,6



Simple and Catenated Spiroalkanes
Sea-Level $(I_{sp})_{opt}$ for Liquids



Mission Performance and I_{sp}

A) From Rocket Equation:

$$\frac{\Delta M_{pl}}{M_{tot}} = -\frac{\Delta M_{tot}}{M_{tot}} = \frac{M_{tot}}{M_{pl}}\left[\frac{\Delta v}{g_o I_{sp}} e^{-\Delta v/g_o I_{sp}}\right]\frac{\Delta I_{sp}}{I_{sp}}$$

1) System Independent–SSTO, LOX/RP-1 to LEO

$$\Rightarrow \frac{\Delta M_{pl}}{M_{tot}} = -\frac{\Delta M_{tot}}{M_{tot}} = k\,\frac{\Delta I_{sp}}{I_{sp}}$$

$$k = \frac{M_{tot}}{M_{pl}}\,0.2$$

2) System Dependent–Atlas First Stage

$$\Rightarrow \frac{\Delta M_{pl}}{M_{tot}} = -\frac{\Delta M_{tot}}{M_{tot}} = k\,\frac{\Delta I_{sp}}{I_{sp}}$$

$$k = 1.8$$

Mission Performance and I_{sp}

B) NASA Study, SSTO (1978)

$$-\frac{\Delta M_{tot}}{M_{tot}} = k\,\frac{\Delta I_{sp}}{I_{sp}}$$

$$k = 2.4$$

C) In-House System Studies:

$$\frac{\Delta M_{pl}}{M_{tot}} = k\,\frac{\Delta I_{sp}}{I_{sp}}$$

Atlas IIAR: $k = 2.5$

Delta III: $k = 1.5$

Zenit: $k = 5.5$

Including Density Effects

A) "Conventional Wisdom"
Performance Metric: $[D^{a}_{prop} I_{sp}]_{opt}$

$$\text{Boost: } a = \frac{2}{3}$$
$$\text{Orbit Transfer: } a = \frac{1}{3}$$
$$\text{Interplanetary: } a = 0$$

B) NASA Study, SSTO (1978)

$$-\frac{\Delta M_{tot}}{M_{tot}} = 2.4\,\frac{\Delta I_{sp}}{I_{sp}} + 0.1\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}}$$

Including Density Effects

C) In-House System Studies:

$$\text{Atlas IIAR:}\ \frac{\Delta M_{pl}}{M_{tot}} = 2.5\,\frac{\Delta I_{sp}}{I_{sp}} + 0.25\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}}$$

$$\text{Delta III:}\ \frac{\Delta M_{pl}}{M_{tot}} = 1.5\,\frac{\Delta I_{sp}}{I_{sp}} + 0.07\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}}$$

$$\text{Zenit:}\ \frac{\Delta M_{pl}}{M_{tot}} = 5.5\,\frac{\Delta I_{sp}}{I_{sp}} + 0.32\,\frac{\Delta \rho_{fuel}}{\rho_{fuel}}$$

RP-1 vs. RG-1

Measured Δh_f (cal/g)	Measured Net Δh_{comb} (BTU/lb)	Specification Net Δh_{comb} (BTU/lb)	Fuel	Measured Density (g/cm^3)	Measured r(H/C)	Sea Level I_{sp} (sec.)
-475	-18640	-18500	RP-1	0.806	2.008	299.8
-508	-18540	-18500	RG-1	0.832	1.991	299.0
-6.9%	-0.53%			+3.2%	-0.85%	-0.27%

- Should Atomic Composition be in the Mil. Spec.?
- How Exactly Should the Effects of Density and Specific Impulse be Simply Modelled?

RP-1 vs. RG-1

Specific Impulse Optimized vs. LOX

RP-1
$CH_{2.008}$

Sea-level (P_c=1000.0 psi, P_e=14.7 psi with Equilibrium Flow):

a	Opt'd $D^a I_{sp}$(sec.)	O/F (by wt.)	T_{chamb} (K)	$D_{prop.}$ (spec. grav.)	I_{sp} (sec.)
0	299.8	2.60	3661	1.028	-
1/3	302.6	2.65	3670	1.029	299.7
2/3	305.6	2.71	3679	1.031	299.4
1	308.8	2.78	3685	1.033	299.0

Vacuum (P_c=1000.0 psi, A_e/A_t=40.0 with Equilibrium Flow):

a	Opt'd $D^a I_{sp}$(sec.)	O/F (by wt.)	T_{chamb} (K)	$D_{prop.}$ (spec. grav.)	I_{sp} (sec.)
0	357.9	2.78	3686	1.033	-
1/3	361.8	2.84	3690	1.034	357.8
2/3	366.0	2.90	3693	1.036	357.5
1	370.4	2.96	3695	1.037	357.0

Specific Impulse Optimized vs. LOX

RG-1
$CH_{1.991}$

Sea-level (P_c=1000.0 psi, P_e=14.7 psi with Equilibrium Flow):

a	Opt'd $D^a I_{sp}$(sec.)	O/F (by wt.)	T_{chamb} (K)	$D_{prop.}$ (spec. grav.)	I_{sp} (sec.)
0	299.0	2.60	3657	1.039	-
1/3	303.0	2.66	3666	1.041	299.0
2/3	307.1	2.71	3674	1.042	298.7
1	311.4	2.76	3680	1.043	298.4

Vacuum (P_c=1000.0 psi, A_e/A_t=40.0 with Equilibrium Flow):

a	Opt'd $D^a I_{sp}$(sec.)	O/F (by wt.)	T_{chamb} (K)	$D_{prop.}$ (spec. grav.)	I_{sp} (sec.)
0	357.1	2.79	3682	1.044	-
1/3	362.3	2.84	3686	1.045	357.0
2/3	367.7	2.88	3688	1.046	356.8
1	373.4	2.93	3690	1.048	356.5

The "Buick Theorem"

Neglect Changes in Pressure Thrust and Assume Δh and Optimum O/F Not Altered by Inert, Dense "Propellant"

$$\frac{[D^a I_{sp}]_{opt+b}}{[D^a I_{sp}]_{opt}} = \frac{\sqrt{1 - f_b}}{\left[1 - f_b\left(\frac{D_{prop}}{D_b} - 1\right)\right]^a}$$

- As $D_b \rightarrow \infty$:

$$\frac{[D^a I_{sp}]_{opt+b}}{[D^a I_{sp}]_{opt}} > 0 \quad \text{for } a > \tfrac{1}{2}$$

- For $D_{prop} = 1$ and $D_b = 8$:

$$\frac{[D^a I_{sp}]_{opt+b}}{[D^a I_{sp}]_{opt}} > 0 \quad \text{for } a > 0.57$$

RP-1 vs. RG-1

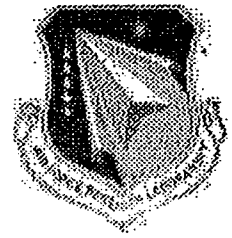
- Is there some f_b for which RP-1 plus a "Buick" give the same $[D^a I_{sp}]$ as RG-1?

  For $a = \frac{1}{3}$: No

  For $a = \frac{2}{3}$: $f_b > 6\%$

  For $a = 1$: $f_b > 2\%$

Conclusions

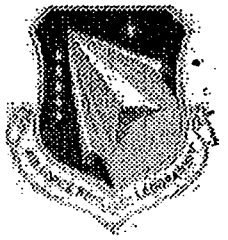


- Minimal Set of Performance-Determining Chemical Parameters Allow Comparison and Search Among Families of Prospective Hydrocarbon Fuels.
- Simple Performance Metrics Constructed from I_{sp} and Fuel Density Allow Rapid "Screening" of Prospective Fuels.
- Caution Must be Exercised with these Simple Metrics.

Future Directions

- Screen Liquid Candidates using Large Molecular Data Bases
- Construct Simple "Benson-Derivatizer"
- Devise Sensible Generic Formulation for Screening Solid Ingredients
- Continue to Examine Simple Performance Metrics

Acknowledgments



- CEA Creators and Maintainers (B. McBride and S. Gordon)
- Beta-Testers (P. Jones)
- Real Rocket Engineers (R. Nichols)
- E.J. Wucherer and P. Carrick